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(54) Title: FORMALDEHYDE FREE 1,3,5-TRIAZINE CARBAMATE CROSSLINKERS AND CURABLE COMPOSITIONS CONTAINING SAME

(57) Abstract: Provided are formaldehyde-free curable compositions containing 1,3,5-triazine carbamates and polyfunctional carbamate reactive material backbone resins, and methods of preparation of such compositions. The compositions may contain a solvent, which solvent may be organic or aqueous. Such curable compositions are particularly suited for use in coatings applications.

FORMALDEHYDE FREE 1,3,5-TRIAZINE CARBAMATE CROSSLINKERS
AND CURABLE COMPOSITIONS CONTAINING SAME

This application claims the benefit of pending U.S.
5 Provisional Application No. 60/168,700, filed December 3,
1999 and pending U.S. Provisional Application No. 60/193,357,
filed March 29, 2000.

FIELD OF THE INVENTION

The present invention relates to formaldehyde free
10 1,3,5-triazine carbamate products that are useable as
crosslinkers in curable coating compositions; and methods of
preparation thereof.

BACKGROUND OF THE INVENTION

Prior art industrial coatings are typically based
15 on backbone resins having active hydrogen groups crosslinked
with various derivatives of amino-1,3,5-triazines. Most
notable among the amino-1,3,5-triazine derivatives are the
aminoplasts, such as the alkoxyethyl derivatives of melamine
and guanamines. While providing excellent results in a
20 number of aspects, the aminoplasts also release formaldehyde
as a volatile by-product during curing. As a result, a need
exists for the coatings industry to reduce the
environmentally undesirable emission of formaldehyde.

One approach for avoiding formaldehyde emissions
25 has been the use of epoxy group-containing compounds cured
with, for example, polyamine and/or polyacid crosslinking
agents. Such systems do not emit formaldehyde on curing.
However, these systems suffer from several disadvantages
including, for example, toxicity of the crosslinkers
30 (particularly the polyamines), poor light stability, and
excessive yellowing of cured films upon exposure to the
elements.

Another approach has been the use of formaldehyde-free crosslinkers, including the 1,3,5-triazine carbamates disclosed in one or more of commonly owned US 4,939,213, US 5,084,541, US 5,288,865, US 5,574,103, EP 0 624 5 577 (corresponding to United States Application Serial No. 08/061,905 (filed May 14, 1993)), EP 0 649 842 (corresponding to United States Application Serial No. 08/138,581 (filed October 15, 1993)), WO 95/30663 (corresponding to United States Application Serial No. 08/239,009 (filed May 6, 1994)), WO 96/04258 (corresponding to United States 10 Application Serial No. 08/286,835 (filed August 5, 1994)), WO 96/11915 (corresponding to United States Application Serial No. 08/324,549 (filed October 18, 1994)), WO 96/15185 (corresponding to United States Application Serial No. 08/340950 (filed November 18, 1994)), and United States 15 Application Serial No. 08/705472 (filed August 29, 1996), all of which are hereby incorporated by reference herein for all purposes as if fully set forth.

While some of the 1,3,5-triazine carbamate (TACT) crosslinkers disclosed above have shown great promise when used as crosslinkers in curable compositions for coatings, 20 they also have some disadvantages. For example, the cured films prepared with these crosslinkers may exhibit slower cure response than films prepared using conventional amino formaldehyde crosslinking agents, and may lead to poor physical and resistance properties, particularly at the 25 elevated temperatures routinely encountered under overbake conditions. Further, despite the excellent films which can be achieved using typical organic solvent based systems, great pressure is currently being exerted on the coatings industry to reduce potentially undesirable emissions of organic compounds including solvent media.

30 Therefore, a need exists for formaldehyde-free coatings that retain the advantages of prior art

carbamate-based systems, but overcome the problems associated with overbake to provide coatings having superior physical and chemical properties to presently known carbamate-based systems. Further, it would be desirable to provide such 5 coatings in a waterborne system, rather than the presently known organic solvent based coating systems. The present invention provides such formaldehyde-free coatings.

SUMMARY OF THE INVENTION

The present invention relates to crosslinker 10 compositions comprising a 1,3,5-triazine carbamate crosslinker.

In one embodiment of the invention, the crosslinker compositions include a blend of at least one 1,3,5-triazine carbamate, particularly a tris(alkoxycarbonylamino) triazine, and at least one polyfunctional carbamate reactive material 15 backbone resin component. The curable composition may be formed by mixing the 1,3,5-triazine carbamate with the polyfunctional carbamate reactive material backbone resin component. The crosslinker and backbone resin components may also be mixed with a cure catalyst, which is typically a 20 quaternary salt, a base, an acid, or an organometallic compound. In addition, the crosslinker compositions optionally contain other optional ingredients, for example, solvents, light stabilizing additives, antioxidants, dyes, dispersants, UV absorbers, heat stabilizers, leveling aids, 25 antifoaming agents and other additives and adjuvants. The curable compositions may be a waterborne coating composition, a powder coating composition, or an organic solvent-containing coating composition.

In another embodiment, the crosslinker compositions include a blend of at least one 1,3,5-triazine carbamate, 30 particularly a tris(alkoxycarbonylamino) triazine, and at least one low molecular weight epoxy resin containing at

least two epoxy functional groups per molecule and having a molecular weight from about 100 g/mol to about 2000 g/mol, or a reaction product thereof. The weight ratio of the at least one 1,3,5-triazine carbamate to the at least one low molecular weight epoxy resin is from about 1:99 to about 5 99:1. Such crosslinker compositions optionally contain from about 1 wt % to about 35 wt % solvent, particularly a solvent that comprises an alcohol having 1 to 8 carbon atoms.

The present invention also relates to curable compositions including at least one compound having a 10 polyfunctional backbone resin having at least one of a polyfunctional epoxy group or polyfunctional hydrogen group; at least one epoxy resin-1,3,5-triazine carbamate crosslinker having a blend of at least one 1,3,5-triazine carbamate, particularly a tris(alkoxycarbonylamino) triazine; at least 15 one low molecular weight epoxy resin containing at least two epoxy functional groups per molecule and having a molecular weight from about 100 g/mol to about 2000 g/mol; and optionally from about 0.001 wt % to about 6 wt % of a basic, acidic, organometallic, or transition metal cure catalyst, or a reaction product thereof. The backbone resin and the 20 crosslinker composition are present in a molar ratio from about 1:5 to about 5:1.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to crosslinker 25 compositions comprising 1,3,5-triazine carbamate crosslinkers. Such compositions were discovered to produce excellent appearance, solvent resistance and gloss characteristics, while reducing the formulating disadvantages inherent to conventional coating systems. In particular, the curable compositions provide crosslinked films or coatings 30 that have acid etch resistance, chemical resistance, resistance to hydrolysis, low toxicity, ease of formulating

stable one-package systems, lower temperature cure requirements, and advantageously eliminate formaldehyde emissions under cure conditions.

5 The present invention relates to crosslinkers containing at least one 1,3,5-triazine carbamate crosslinker, which do not release formaldehyde when used in curable compositions. In particular, the formaldehyde-free crosslinkers are a blend of at least one 1,3,5-triazine carbamate and at least one polyfunctional carbamate reactive material backbone resin component.

10 The present invention also relates to curable compositions which contain at least one polyfunctional backbone resin component and at least one crosslinker composition. In particular, the curable compositions comprise at least one of an epoxy, hydroxyl, or carboxyl functionalized backbone resin and at least one 1,3,5-triazine carbamate crosslinker. In addition, the crosslinker compositions may also contain one or more other ingredients, for example, organic and aqueous solvents, cure catalysts, light stabilizing additives, antioxidants, antifoaming agents and other additives and adjuvants.

15 The present invention also relates to a method for preparing such crosslinkers, as well as such curable compositions comprising at least one polyfunctional carbamate reactive material backbone resin component, at least one 1,3,5-triazine carbamate crosslinker, and, optionally, a cure catalyst.

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The Crosslinker Compositions

30 The crosslinker compositions of the present invention include at least one 1,3,5-triazine carbamate and at least one polyfunctional carbamate reactive material backbone resin component. The blend of 1,3,5-triazine carbamate and the polyfunctional carbamate reactive material

backbone resin component provides a 1,3,5-triazine crosslinker composition that does not emit formaldehyde under cure conditions.

In a preferred embodiment, the crosslinker compositions are solids that are substantially organic solvent free and the weight ratio of 1,3,5-triazine carbamate to polyfunctional carbamate reactive material backbone resin component is from about 1:99 to about 99:1, and preferably from about 25:75 to about 75:25.

In another preferred embodiment, the crosslinker compositions are liquids that include an organic solvent in an amount from about 1 wt % to about 35 wt%, more preferably from about 10 wt % to about 30 wt%. In addition, the crosslinker compositions include a combination of the 1,3,5-triazine carbamate and the polyfunctional carbamate reactive material backbone resin component in an amount from about 65 wt % to about 99 wt%, preferably from about 70 wt % to about 90 wt %. The weight ratio of 1,3,5-triazine carbamate to polyfunctional carbamate reactive material backbone resin component is from about 1:99 to about 99:1, and preferably from about 25:75 to about 75:25.

In yet another preferred embodiment, the crosslinker compositions are liquids that include water as a solvent in an amount from about 1 wt % to about 35 wt%, more preferably from about 10 wt % to about 30 wt%. In addition, the crosslinker compositions include a combination of the 1,3,5-triazine carbamate and the polyfunctional carbamate reactive material backbone resin component in an amount from about 65 wt % to about 99 wt%, preferably from about 70 wt % to about 90 wt %. The weight ratio of 1,3,5-triazine carbamate to polyfunctional carbamate reactive material backbone resin component is from about 1:99 to about 99:1, and preferably from about 25:75 to about 75:25.

1,3,5-Triazine Carbamate Monomers:

As used herein, "1,3,5-triazine carbamate" means a monomeric compound based on a 1,3,5-triazine core having on average at least two hydrocarbyloxycarbonylamino groups attached to the triazine ring. Such 1,3,5-triazine carbamates and methods for preparing the same are known, for example, from the previously incorporated commonly owned US 4939213, US 5084541, US 5288865, US 5,556,971, US 5,565,243, US 5574103, EP-A-0624577 (corresponding to United States Application Serial No. 08/061,905 filed May 14, 1993),

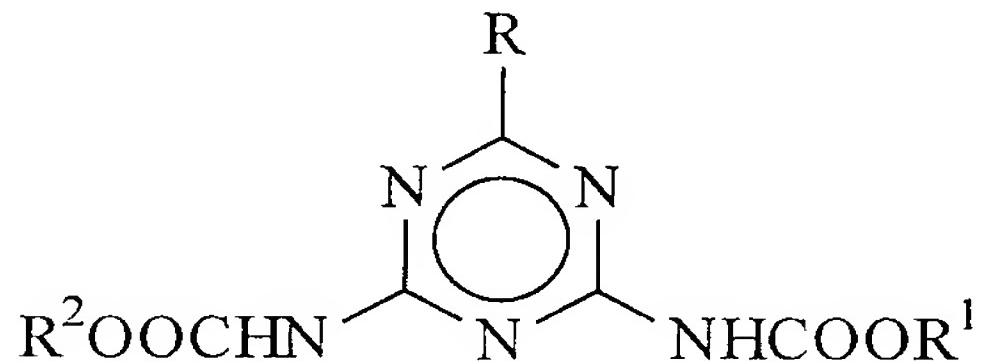
5 EP-A-0649842 (corresponding to United States Application Serial No. 08/138,581, filed October 15, 1993), WO 95/30663 (corresponding to United States Application Serial No. 08/239,009 (filed May 6, 1994)), WO 96/04258 (corresponding to United States Application Serial No. 08/286,835 (filed

10 August 5, 1994)), WO 96/11915 (corresponding to United States Application Serial No. 08/324,549 (filed October 18, 1994)) and WO 96/15185 (corresponding to United States Application Serial No. 08/340,950 (filed November 16, 1994)), and reference may be had thereto for further details.

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Preferably, the 1,3,5-triazine carbamate crosslinker products of the invention are formed from 1,3,5-triazine carbamates of the general formula:

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wherein R is selected from the group consisting of -NHCOOR³,

hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbylthio,

amido, sulfonamido, amino, hydrocarbylamino,

30 dihydrocarbylamino and cyclic amino; and wherein each R¹, R²

and R³ is independently selected from the group consisting of hydrocarbyl and hydrocarbyloxyhydrocarbyl.

The term "hydrocarbyl", as used herein, broadly refers to a monovalent hydrocarbon group in which the valency is derived by abstraction of a hydrogen from a carbon atom.
5 Hydrocarbyl includes, for example, straight and branched chain aliphatics, cycloaliphatics, aromatics, and mixed character groups, e.g., aralkyl and alkaryl. Hydrocarbyl also includes such groups with internal unsaturation and activated unsaturation. More specifically, hydrocarbyl
10 includes, but is not limited to, such groups as alkyl, cycloalkyl, aryl, aralkyl, alkaryl, alkenyl, cycloalkenyl and alkynyl, preferably having up to 24 carbon atoms. A hydrocarbyl may optionally contain one or more carbonyl groups, which are included in the carbon count, and/or a heteroatom or heteroatoms, such as at least one oxygen,
15 sulfur, nitrogen or silicon, in the chain or ring.

Preferably, R is selected from the group consisting of -NHCOOR³, hydrogen; a hydrocarbyl group having from 1 to 20 carbon atoms, such as alkyl, e.g., methyl and butyl, cycloalkyl, e.g., cyclohexyl, alkenyl, e.g., vinyl, aryl,
20 e.g. phenyl, aralkyl, e.g., benzyl, and the like; a hydrocarbyloxy group having 1 to 20 carbon atoms, such as alkoxy, e.g., methoxy, aryloxy, e.g., phenoxy, and the like; hydrocarbylthio groups having 1 to 20 carbon atoms, such as methylthio, phenylthio and the like; amido groups, such as acetamido; sulfonamido groups, such as benzenesulfonamido; an
25 amino group, e.g., -NH₂; hydrocarbylamino groups having 1 to 20 carbon atoms, such as methylamino, butylamino and the like; dihydrocarbylamino groups having 2 to 40 carbon atoms, such as dimethylamino; and cyclic amino groups, such as pyrrolidino, piperidino, morpholino, azepino, and the like.
30 Compounds wherein R is -NHCOOR³ are especially preferred.

- Preferably, R¹, R² and R³ are independently hydrocarbyl groups having 1 to 20 carbon atoms such as alkyl, e.g., methyl and butyl, cycloalkyl, e.g., cyclohexyl, alkenyl, e.g., vinyl, aryl, e.g. phenyl, aralkyl, e.g., benzyl, and the like and hydrocarbyloxyhydrocarbyl groups having 2 to 40 carbon atoms with the hydrocarbyl group being as described above. In addition, these groups may also contain substituents, such as a halogen atom, a cyano group, a sulfoxide group, a sulfone group, a carbonyl group, an ester group, or an amide group.
- More preferably, R¹, R² and R³ are independently aliphatic alkyl or alkenyl having 1 to 8 carbon atoms, cyclic alkyls and alkenyls having 4 to 12 carbon atoms, alkoxyalkyls having 2 to 16 carbon atoms, and aryl and alkaryls having 6 to 18 carbon atoms. Examples of the most preferred R¹, R² and R³ include methyl, ethyl, propyl, n-butyl, i-butyl, t-butyl, pentyl, hexyl, cyclohexyl, heptyl, octyl, ethylhexyl, allyl, ethoxyethyl, 1-methoxy-2-propyl, phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, dimethylphenyls, 2-chlorophenyl, 3-chlorophenyl, 4-chlorophenyl and mixtures thereof.
- The most preferred 1,3,5-triazine carbamate crosslinkers for use in this invention are those wherein R is -NHCOOR³, and R¹, R² and R³ are independently alkyls having 1 to 8 carbon atoms, and particularly methyl and/or butyl, which includes not only tris-(butoxycarbonylamino)-1,3,5-triazine and tris-(methoxycarbonylamino)-1,3,5-triazine, but also the mixed tris-substituted (methoxy/butoxycarbonylamino)-1,3,5-triazine systems. Preferred examples of the latter include 1,3,5-triazine carbamate crosslinkers having a methyl to butyl molar ratio in the range of from about 0.25:1 to about 1.5:1.

The Backbone Resin Component

The backbone resin component comprises a carbamate reactive material including, for example, a polyfunctional epoxy group containing material, a polyfunctional hydroxy group containing material, or a mixture thereof.

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The polyfunctional epoxy group containing material usable as a backbone resin component in the curable compositions of the present invention typically contains at least two, and, preferably, more than two epoxy functionalities per molecule. Epoxy compounds particularly

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suitable for use in the present invention as co-crosslinkers are low molecular weight polyfunctional epoxy resins, wherein the term "low molecular weight," means a molecular weight from about 100 g/mol to about 2000 g/mol, preferably from about 200 g/mol to about 800 g/mol, and more preferably from about 300 g/mol to about 600g/mol. It is also preferred that

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the low molecular weight epoxy resin is either aromatic or aliphatic.

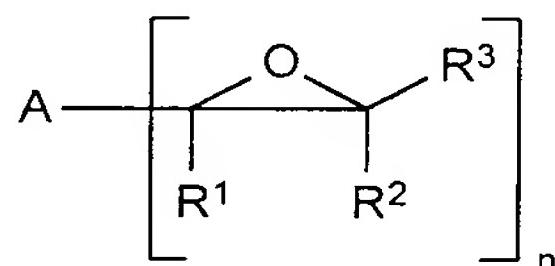
The polyfunctional epoxy group containing material usable as a backbone resin component in the curable compositions of the present invention include materials that

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are monomeric, oligomeric, polymeric, or a mixture thereof.

The polyfunctional epoxy group containing material may be generically represented by the formula:

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wherein A is an n-functional monomeric, oligomeric or polymeric anchor to which n epoxy groups are pendently

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attached; wherein n is at least 2; and wherein R¹, R² and R³ are the same or different, and each is independently selected

from the group consisting of hydrogen, alkyl, aryl, and aralkyl.

The monomeric polyfunctional epoxy group containing materials include the following: diepoxides, such as diglycidyl bis-phenol-A, vinyl cyclohexene diepoxide, and the like; triepoxides, such as tri-(4-glycidyl oxyphenyl)methane; and higher polyfunctional epoxides, such as glycidylated pentaerythritol and sorbitol. The oligomeric polyfunctional epoxy group containing materials include oligomeric forms of the monomeric materials, oligomers of diepoxides, such as low molecular weight bis-phenol-A oligomers, prepolymers thereof, reaction products of amines with diepoxides, and the like. The polymeric polyfunctional epoxy group containing materials include polymers of epoxy group containing unsaturated monomers and copolymers thereof, such as glycidyl acrylate and glycidyl methacrylate, with unsaturated co-monomers that do not contain epoxy groups, such as methyl acrylate, ethyl acrylate, butyl acrylate, ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethylhexyl methacrylate, styrene, methyl styrene, vinyl acetate, allyl alcohol, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, and the like. The copolymerization reaction may be carried out by known methods such as that described in U.S. Patent Nos. 3,787,521 and 4,181,642 and European Patent Nos. 0 480 120 and 0 256 369. Examples of monomeric difunctional epoxides include 4-vinyl-1-cyclohexene diepoxide, a product of Dow Chemical, Inc., Midland, MI, 1,2,5,6- diepoxyoctane, 1 ,2,7,8-diepoxyoctane, dicyclopentadiene diepoxide, 1 ,4-divinyl benzene diepoxide, cyclohexene-4-methyl cyclohexene-4-carboxylate diepoxide, and the like. Examples of glycidylated diol type polyfunctional epoxy group containing materials include hexane diol diglycidyl ether, ethylene glycol diglycidyl ether,

diethylene glycol diglycidyl ether, triethylene glycol diglycidyl ether, and the like. Examples of glycidylated bis-phenol-A type polyfunctional epoxy group containing materials include the substantially monomeric Epon® 828 resin, a product of Shell Chemical Company, Houston, TX, having an equivalent weight in the range of 185 to 192 and oligomeric forms thereof. Examples of glycidylated polyhydroxy compound type polyfunctional epoxy group containing materials include the substantially monomeric glycidylated sorbitol known as Synocure® 888 H resin, a product of Cook Composites and Polymers Company, Port Washington, Wisconsin. Examples of glycidyl methacrylate copolymer type polyfunctional epoxy group containing materials include Synthacryl® VCS 1436 resin, a product of Hoechst-Celanese Corporation, Charlotte, NC, Estron® GMA-252 resin (Mw: 8300; EW: 250; Tg: 36), a product of Estron Chemicals, Calvert City, KY, Almatex® PD 6100 (Mw: 12500; EW: 1030; Tg: 63), Almatex® PD 6300, Almatex® PD 7110, Almatex® PD 7210, Almatex® PD 7310, Almatex® PD 7610 (Mw: 7000; EW: 510; Tg: 45) and Almatex® PD 1700 resins, products of Mitsui Toatsu Company, Inc. of Japan, available from Anderson Development Company, Adrian, MI, and Blemmer® CP-15 (Mw: 12300; EW: 1000; Tg: 63), Blemmer® CP-30 P (Mw: 10300; EW: 530; Tg: 62) and Blemmer® CP-5 SA (Mw: 10100; EW: 3000; Tg: 96) resins, products of Nippon Oil and Fat Corporation.

Polyfunctional hydroxy group containing materials, polyfunctional carboxyl group containing materials and polyfunctional hydroxy group and carboxyl group containing materials may be also used as a backbone resin component, either alone or in combination with the polyfunctional epoxy group containing materials in the curable compositions of the invention. These materials are generally well known to those skilled in the art and have been described in the previously incorporated US 4,939,213, US 5,084,541, US 5,288,865,

EP 0 624 577 (corresponding to United States Application Serial No. 08/061,905 (filed May 14, 1993)), EP 0 649 842 (corresponding to United States Application Serial No. 08/1 38,581 (filed October 15, 1993)), WO 95/30663 (corresponding 5 to United States Application Serial No. 08/239,009 (filed May 6, 1994)), WO 96/04258 (corresponding to United States Application Serial No. 08/286,835 (filed August 5, 1994)), and WO 96/11915 (corresponding to United States Application Serial No. 08/324,549 (filed October 18, 1994)).

- The polyfunctional hydroxy group containing 10 materials useful in the invention contain at least two, and, preferably, more than two hydroxy groups. The preferred polyfunctional hydroxy group containing materials are acrylic or polyester backbone resins. Although TACT exhibits limited ability to form self-condensation products, effective difunctional polyester resin/TACT systems can be formulated 15 by the addition of an epoxy resin and a suitable catalyst. Such systems exhibit the crosslinking density necessary to produce enhanced coating properties. Illustrative examples of the preferred polyfunctional hydroxy group containing materials include acrylic resins, which may be obtained by 20 the copolymerization of acrylic or methacrylic esters with hydroxyfunctional acrylic or methacrylic esters, such as hydroxyethyl acrylate or methacrylate, optionally with simultaneous use of additional vinyl compounds such as, for example, styrene. Illustrative examples of the 25 polyfunctional hydroxy group containing materials also include polyester resins which may be obtained, for example, by the reaction of polycarboxylic acids with excess quantities of polyhydric alcohols. Additionally, suitable polyfunctional hydroxy group containing resins also include polyurethane prepolymers, alkyds, as well as hydroxy group 30 containing epoxy prepolymers such as those resulting from the reaction of a polyfunctional epoxy group containing compound

with an amine or with a polyfunctional carboxylic acid derivative.

In general, such resins may have pendent or terminal hydroxyl functionalities and preferably have the following characteristics: weight average molecular weights (Mw) of from about 750 to about 7000, and, more preferably, from about 2000 to about 5000; and hydroxyl numbers of from about 20 to about 100 mg KOH/g resin, more preferably from about 25 to about 60 mg KOH/g resin, and especially from about 25 to about 40 mg KOH/g resin. For waterborne coatings applications, polyfunctional hydroxy group containing materials having thereon aqueous dispersion promoting groups such as carboxylic or sulfonic functionalities and higher molecular weights are generally usable. Other suitable hydroxyl functional resins will be readily recognized by those of ordinary skill in the art.

Examples of the polyfunctional hydroxy group containing material include JONCRYL® 540 acrylic resin polymer (S.C.Johnson & Sons, Racine, WI), JONCRYL® 500 acrylic resin (S.C.Johnson & Sons, Racine, WI), ACRYLOID® AT-400 acrylic resin (Rohm & Haas, Philadelphia, PA), CYPLEX® 1531 polyester resin (Cytec Industries, West Paterson, NJ), CARGILL 3000 and 5776 polyester resins (Cargill, Minneapolis, MN), TONE® polyester resin (Union Carbide, Danbury, CT), K-FLEX® XM-2302 and XM-2306 resins (King Industries, Norwalk, CT), CHEMPOL® 11-1369 resin (Cook Composites and Polymers (Port Washington, WI), RHOPLEX®AC-1024 acrylic emulsion resin (Rohm & Haas, Philadelphia, PA), XC® 4005 water reducible acrylic resin (Cytec Industries, West Paterson, NJ), CRYLCOAT® 3494 solid hydroxy terminated polyester resin (UCB CHEMICALS USA, Smyrna, GA), RUCOTE® 101 polyester resin (Ruco Polymer, Hicksville, NY), JONCRYL® SCX-800-A and SCX800-B hydroxyfunctional solid acrylic resins (S.C.Johnson & Sons, Racine, WI), ALFTALAT® AN 745 hydroxyfunctional polyester

resin, a product of Hoechst Corporation, and the like. Solid polyfunctional hydroxy group containing materials are suitable for use in powder coatings. For solvent borne coatings, liquid polyfunctional hydroxy group containing materials are preferred. However, a solid polyfunctional hydroxy group containing material may be used in cases when the solids are soluble in the solvent used in a particular formulation.

Other Ingredients

In addition to the crosslinkers and backbone resins described in detail above, the curable compositions of the present invention may optionally comprise a variety of additional ingredients. One such ingredient is a cure catalyst for increasing the cure rate, and, thereby, reducing the cure temperature and/or cure time of the 1,3,5-triazine carbamate crosslinked systems described herein. Suitable catalysts include quaternary salt catalysts, basic catalysts, organometallic catalysts, transition metal compounds and acidic catalysts. The type of catalyst used may be readily determined by one of ordinary skill in the art, depending on the curable composition. For example, an acid catalyst is suitable for use in curing a curable composition including an epoxy group-containing resin.

Suitable basic catalysts include, but are not limited to, quaternary ammonium and phosphonium salts, strong nitrogenous bases, and inorganic bases. Typically, the basic catalysts include, for example, primary amines; secondary amines; tertiary amines; imines; amidines; guanidines; trialkyl phosphines; alkali metal salts, e.g., salts of lithium, sodium, or potassium; quaternary ammonium salts; quaternary phosphonium salts; quaternary sulfonium salts, or mixtures thereof. The basic salts described herein each have one or more counter ions, such as hydroxide, C_1-C_{20} alkoxide,

C_6-C_{20} aryloxide, carboxylate, carbonate, or mixtures thereof. Preferably, the basic catalysts include quaternary ammonium hydroxides, quaternary ammonium alkoxides, quaternary ammonium carboxylates, quaternary ammonium carbonates, trialkyl amines, triaryl amines, alkyldiaryl amines, dialkylaryl amines, cyclic amines, bicyclic amines, polycyclic amines, heteroaromatic amines, alkylated guanidines, or mixtures thereof. More preferably, the basic catalysts include benzyl trialkylammonium hydroxides, 4-dimethylaminopyridine, 4-pyrrolidinopyridine, 4-

5 piperidinopyridine, 4-morpholinopyridine, 1,4-diaza-(2.2.2)-bicyclooctane, tetramethylguanidine, or mixtures thereof.

Useful acidic catalysts include Lewis acids, sulfonic acids, such as p-toluene sulfonic acid or dodecyl benzene sulfonic acid, aryl and alkyl acid-phosphates and pyrophosphates, carboxylic acids, sulfonimides and mineral acids. Latent acidic catalysts, such as amine-blocked p-toluene sulfonic acid or amine-blocked dodecyl benzene sulfonic acid, are included within the meaning of acidic catalysts.

Suitable organometallic catalysts include organotin compounds. Preferably, the organometallic catalysts include dibutyltin di-2-ethylhexanoate, dibutyltin diisooctyl maleate, dibenzyltin di-2-ethylhexanoate, dibutyltin dilaurate, dimethyltin dilaurate, tetrabutyl diacetoxy distannoxane, tetramethyl diacetoxy distannoxane, tetrapropyl diacetoxy distannoxane, dibutyltin dichloride, or mixtures thereof.

Cure catalysts, when used, are present in an amount ranging from about 0.001 wt % to about 6 wt %, preferably from about 0.01 wt % to about 4 wt %, more preferably from about 0.1 wt % to about 3 wt %, based on the combined weight

20 of the backbone resin and crosslinker components, i.e., total resin solids.

The present curable compositions may also contain a solvent of the type typically found in coatings applications, including, for example, alcohols, ketones, esters, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, and the like.

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More preferred organic solvents include, but are not limited to, ethers, such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether and triethylene glycol dimethyl ether; amides, such as N,N-dimethyl acetamide; N-methyl pyrrolidone; N,N-dimethyl formamide; 10 hexamethyl phosphoramide; hydrocarbons, such as toluene, hexane, and xylene; sulfones, such as dimethyl sulfone; sulfonate; esters, such as methyl acetate, ethyl acetate and ethyl formate; lower alcohols; and mixtures thereof. Alcohols of 1 to 8 carbon atoms are preferred, as well as 15 isomers thereof and mixtures thereof. A more preferred alcohol is n-butanol. Also suitable are solvents having a plurality of functionalities, such as ethylene glycol monomethyl ether, methoxypropyl acetate, hydroxypropyl acetate, or mixtures thereof.

In waterborne coating applications, the curable 20 compositions may contain, in addition to water, a co-solvent and an aqueous dispersion promoting material, such as ethylhexanol, Texanol® (a C8-hydroxyalkyl ester of methylpropionic acid commercially available from Eastman Chemical Company), surfactants, and other related materials.

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Other optional ingredients may be used depending on the particular application. For example, well known auxiliaries and additives typically utilized in the coatings industry include foam inhibitors; leveling aids; pigments; dispersants, e.g., pigment dispersing aids; dyes; UV absorbers, including hydroxy aryl triazine types (e.g., 30 CYAGARD UV 1164, Cytec Industries Inc., Stamford, CT), benzotriazole types and benzophenone types; heat stabilizers;

other stabilizing additives, such as antioxidants; and hindered amine light stabilizers, such as SANDUVOR 3055 and 3058 (Clariant Corp., Charlotte, NC). Other such optional ingredients are known to those of ordinary skill in the art.

5 In particular, the stabilization of coatings and other curable compositions with UV absorbers, hindered amine light stabilizers and/or other types of light stabilizers are disclosed in U.S. Patent Nos. 4,426,471, 4,344,876, 4,619,956, 5,106,891, 5,322,868, and 5,461,151; and in European Patent Application Nos. EP-A-434,608 and EP-A-
10 704,437.

Preparation and Uses of the Coatings

The crosslinker compositions of the present invention are typically prepared by admixing at least one 1,3,5-triazine carbamate, at least one polyfunctional carbamate reactive material backbone resin component, and optionally at least one solvent or another ingredient, at a temperature, pressure, and for a length of time sufficient to produce a substantially homogenous crosslinker composition.

15 The components for the crosslinker compositions may be admixed in any order. The term "admix," as used herein, includes any act of combining, mixing, or blending of different substances, ingredients, or components.

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Coatings prepared in accordance with the present invention may be prepared by combining a solvent, the components of the curable composition of the invention, and any optional ingredients, if present, in any convenient order. Generally, the crosslinker to backbone resin weight ratio is not critical. However, it is preferred that when these ingredients comprise a major portion of the coating composition, they be present in a crosslinker to backbone
25 resin weight ratio in the range of from about 0.05:1 to about 1:1, and especially in the range of from about 0.15:1 to
30

about 0.35:1. When polyfunctional co-crosslinkers are also employed, or when a plurality of backbone resins are employed, it is preferred that the overall crosslinker component to overall backbone resin component weight ratio be within the same range of from about 0.05:1 to about 1:1, and especially in the range of from about 0.15:1 to about 0.35:1.

The substantially homogeneous crosslinker compositions and the backbone resin component may be combined to form curable compositions according to the invention suitable for numerous uses including, for example, coatings, adhesives, decorative laminated boards, and crosslinked molded articles, such as engineering composites.

A preferred use of these curable compositions is in the coatings field. In particular, the curable coating compositions of the invention may be formulated for use in a variety of applications, including original equipment manufacturing (OEM), such as automotive coatings, general industrial coatings, industrial maintenance coatings, architectural coatings, can coatings, coatings for wire, appliance coatings, coatings for automotive parts, furniture coatings, pipe coatings, machinery coatings, and the like.

The curable coating compositions may also replace 1K urethane coatings in applications including base coats and top coats for acid etch resistant automotive finishes, powder coatings, and coil coatings.

Curable coating compositions can also be readily prepared by methods that are known to those of ordinary skill in the art. Typically, the preparation of curable compositions involves admixing the backbone resin component and the crosslinker component in amounts such that the molar ratio of the reactive functionality of the crosslinker component to the reactivity of the backbone resin component is from about 1:5 to about 5:1, preferably from about 1:2 to about 3:1, and more preferably from about 4:5 to about 8:5.

Any conventional type of coating may be prepared using the curable compositions described herein, including organic solvent-based liquid coatings, waterborne coatings, and powder coatings. Those of ordinary skill in the art may readily determine the compositions of these coatings, including the relative amounts, depending on the intended use and desired coating characteristics. The curable compositions may optionally include an organic solvent, water, and other additional ingredients, such as foam inhibitors, leveling aids, pigments, pigment dispersing aids, dyes, UV stabilizers, flow promoters, anti-sag agents, anti-cratering additives and other stabilizing additives.

Organic solvent-based liquid coating compositions of the present invention may be prepared by any method known to those of ordinary skill in the art, for example, by adding the components of the curable composition and optional ingredients, if present, to an organic solvent in any particular order. For such coatings, a liquid backbone resin component is preferred, however, solid backbone resin components may be used, particularly in cases when the solid backbone resin components are soluble in the particular organic solvent used. These compositions are formulated to produce a solids content level suitable for convenient application with minimal material loss, typically at a solids content level from about 20 wt % to about 85 wt %, preferably from about 35 wt % to about 80 wt %, more preferably 45 wt % to about 75 wt %, depending on the application chosen.

Waterborne coating compositions of the present invention may be prepared by any method known to those of ordinary skill in the art by combining the components of the curable composition in any particular order. For example, such compositions are preferably prepared by homogeneously mixing the curable composition components with a surface active material to form a dispersible composition followed by

dispersing the dispersible composition in an aqueous medium, which may include water or water-miscible co-solvents, to ease dispersion or adjust viscosity. The polyfunctional backbone resins may additionally have aqueous dispersion promoting groups that generate anions upon neutralization with, for example, carboxylic or sulfonic functionalities, within the resin structure, such as those disclosed in PCT Publication Nos. WO 96/15185 and WO 97/08235, as well as British Patent No. GB 1,530,022, European Application Nos. EP-A-568,134 and EP-A-663,413, and U.S. Patent Nos. 5,075,370 and 5,342,878, each disclosure being incorporated herein by express reference thereto. Especially preferred are carboxylic groups. The waterborne coating compositions may be formulated to contain various solids contents, typically from about 20 wt % to about 75 wt % solids, preferably 25 wt % to about 60 wt %, more preferably 30 wt % to about 50 wt %, depending on the method of application chosen.

The anion-generating groups present on the backbone resin must be neutralized, at least in part, to render the backbone resin water dispersible. Suitable neutralizing agents to generate such anions are known to those of ordinary skill in the art and include, for example, organic and inorganic bases, such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, primary amines, secondary amines, and tertiary amines. Tertiary amines are preferred as neutralizing agents.

In another embodiment, waterborne coating compositions may be prepared by adding an aqueous dispersion-promoting agents to the curable compositions of the present invention. Such aqueous dispersion-promoting agents are known to those of ordinary skill in the art and include organic compounds with an alkyl chain or aromatic group substituted with a hydrophilic moiety. Preferred aqueous dispersion-promoting agents include long chain aliphatic

alcohols, e.g., ethylhexanol, octanol, dodecanol; benzyl alcohol and other aromatic alcohols; ester alcohols, e.g., hydroxyalkyl esters of alkanoic acids; and the like. More preferred are long chain alkyl alcohols having at least 8 carbon atoms, such as C₈-hydroxyalkyl esters of 5 methylpropionic acid, e.g., TEXANOL (Eastman Chemical Company, Kingsport, TN).

In yet another embodiment, waterborne coating compositions may be from a pre-mix formed by adding optionally at least one polyfunctional carbamate reactive 10 material backbone resin component and/or a cure catalyst to a 1,3,5-triazine carbamate, admixing the pre-mix with an emulsion polymer, and optionally adjusting the viscosity of the resulting composition by the addition of water. The preferred polyfunctional carbamate reactive material backbone 15 resin component is a small molecular weight polyfunctional epoxy resin, the preferred catalyst is an amine, and the preferred emulsion polymer is an acrylic emulsion polymer.

Powder coating compositions of the present invention may be prepared by any method known to those of ordinary skill in the art, for example, by dry mixing the 20 curable composition components in a mixer or blender followed by compounding in an extruder and granulating, grinding, and sifting through a screen to obtain a powder size having suitable mesh size for powder coating. For powder coating applications, curable compositions containing solid 25 crosslinker and backbone resin are preferred. Alternatively, some or all of the components may be dissolved in a solvent, such as methylene chloride, and spray dried by techniques known to those of ordinary skill in the art. In another embodiment, it is preferable to masterbatch the crosslinker and the backbone resin prior to mixing in any optional 30 components desired in the curable composition.

The present coating compositions are utilized by applying the curable compositions to a substrate followed by curing to form crosslinked films. Liquid coatings may be applied or contacted to a substrate by any method known to those of ordinary skill in the art, for example, by dipping, spraying, padding, brushing, flowcoating, electrocoating, or electrostatic spraying. After applying or contacting, the solvent, (e.g., organic solvent or water) is allowed to at least partially evaporate to produce a uniform coating on the substrate. Thereafter, the compositions may be further cured by application of heat at a temperature and for a length of time sufficient to produce substantially fully cured coatings. Powder coatings may be applied or contacted to a substrate, for example, by any method known to those of ordinary skill in the art, for example, by powder gun, electrostatic deposition, or deposition from a fluidized bed. After deposition, the powder is typically heated to a temperature sufficient to cause the particles to soften, melt, flow, and cure.

Full curing of the present curable compositions requires typically cure temperatures from about 25°C to about 450°C. For liquid coating applications, the full cure temperature is preferably from about 70°C to about 180°C, more preferably from about 85°C to about 155°C, and most preferably from about 100°C to about 140°C. For powder applications, the cure temperature is preferably from about 110°C to about 230°C, more preferably from about 150°C to about 220°C, most preferably from about 170°C to about 200°C. For coil applications, the full cure temperature is preferably from about 250°C to about 450°C, more preferably from about 300°C to about 425°C. Cure time is typically from about 1 second to about 45 minutes and will vary depending on the temperature and materials chosen for cure. For example, a fully cured coil coating may be obtained by either curing a

curable composition at 260°C for 1 minute or by curing at 417°C for 20 seconds. A typical cure time for liquid and powder coatings is from about 5 minutes to about 30 minutes.

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The invention is further defined by reference to the following examples describing the preparation of the compounds and compositions used in the present invention, as well as their utility. It will be apparent to those skilled in the art that many modifications, both to materials and 10 methods, may be practiced without departing from the purpose and interest of this invention. In the following examples, all amounts are expressed as parts by weight, unless otherwise stated.

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EXAMPLE 1: Curable Compositions of Epoxy resin-TACT Crosslinker and Epoxy Functional Acrylic Backbone Resin

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A curable composition containing an epoxy functional backbone resin was prepared by combining a low molecular weight epoxy resin co-crosslinker, 50 wt % TACT co-crosslinker in n-butanol (CYLINK® 2000 Crosslinking Agent; Cytec Industries, Inc., West Paterson, NJ), and the epoxy functional backbone resin, HELOXY Modifier 71 (Shell Chemical Company, Houston, TX), along with 20 wt % benzyltrimethylammonium acetate catalyst in n-butanol, and 10 % Dow Corning Paint Additive 57 (DC#57, Dow Corning Corp., Midland, MI) in n-butanol in the relative amounts shown in Table 1. The curable composition was then applied to the substrate, iron phosphate treated cold roll steel panel, by using a #40 wire cator applicator, and subsequently cured at 135°C for 30 minutes.

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The resulting coating has a film thickness of 1.9 mm, a Knoop hardness (KHN₂₅) of 3.0, MEK rubs of 50/200+, a direct impact measurement of 160+ lbs, and a reverse impact

measurement of 160+ lbs, each of which are shown in Table 1. Knoop hardness is a measurement of the hardness of a film, determined by measuring the extent of an indent made with a diamond tip that is dropped at a constant rate onto the coating. Solvent resistance was measured by methyl ethyl ketone (MEK) double rubs "to mar" and "to remove" the coating. MEK double rubs are measured by two solvent resistance values, the first is the number of rubs to mar the coating, and the second is the number of rubs to remove the coating. When only one value is shown, the number shown is the number of rubs to remove it since the coating did not mar.

Table 1: Curable Composition (Epoxy resin-TACT crosslinker and Epoxy Functional Backbone Resin)

	HELOXY Modifier 71	50.8
15	HELOXY Modifier 48	17.8
	CYLINK® 2000 Crosslinking Agent*	62.7
	Benzyltrimethylammonium acetate, 20 wt % in n-butanol	7.5
20	DC#57 Paint Additive, 10 % in n-butanol	0.5
	Substrate	Iron phosphate treated cold roll steel panel
	Bake Schedule	135°C for 30 minutes
	Film thickness, mm	1.9
25	Film Hardness, KHN ₂₅	3.0
	MEK rubs	50/200+
	Direct Impact, lb	160+
	Reverse Impact, lb	160+

* TACT, 50 wt % in n-butanol

EXAMPLE 2: Curable Compositions of Epoxy resin-TACT Crosslinker and Hydroxyl Functional Acrylic Backbone Resin

The curable composition containing a hydroxyl functional backbone resin was prepared by combining the low molecular weight epoxy resin, EPON Resin 825 (Shell Chemical Company, Houston, TX), CYLINK® 2000 Crosslinking Agent (Cytec Industries, Inc., West Paterson, NJ), and the hydroxyl functional acrylic backbone resin, DORESCO TA39-21 Acrylic Resin (Dock Resins, Linden, NJ), along with 1.5% 4-dimethylaminopyridine (DMAP) catalyst as a 20% solution in 1:1 xylene/isopropanol and 1:1:1 xylene/MIBK/ARCOSOLV PM Acetate (Arco Chemical, Philadelphia, PA) in the relative amounts shown in Table 2. The curable compositions were applied to the substrate, iron phosphate treated cold roll steel panel, by using a #40 wire cator applicator, and subsequently cured at various cure temperatures ranging from 100°C to 140°C for 30 minutes.

The resulting coatings have physical properties shown in Table 3, in which the coatings exhibit increases in film hardness from 10.5 to 15.4 and increases in MEK rubs from 1/40 to 200+ as the curing temperature is increased from 100°C to 140°C.

Table 2: Curable Composition (Epoxy resin-TACT crosslinker and Hydroxyl Functional Backbone Resin)

	DORESCO TA39-21 Acrylic Resin	19.3
25	EPON Resin 825	6.0
	CYLINK® 2000 Crosslinking Agent	17.1
	4-Dimethylaminopyridine, 20 wt % in 1:1 xylene/isopropanol	1.5
30	1:1:1 ratio of Xylene/methyl isobutyl ketone (MIBK)/ARCOSOLV PM Acetate	6.1

Substrate	Iron phosphate treated cold roll steel panel
Cure Schedule	100-140°C for 30 minutes

5 Table 3: Physical Properties of Curable Composition

Cure Schedule	100 °C/30 min	110 °C/30 min	125 °C/30 min	140 °C/30 min
Film Thickness, mm	1.7	1.8	1.8	1.8
Film Hardness, KHN ₂₅	10.5	13.4	14.0	15.4
MEK rubs	1/40	100/200+	200+	200+

15 EXAMPLE 3: Curable Compositions of Epoxy resin-TACT Crosslinker and Carboxyl Functional Acrylic Backbone Resin

The curable composition containing a carboxyl functional backbone resin was prepared by combining the low molecular weight epoxy resin, EPON Resin 825 (Shell Chemical Company, Houston, TX), CYLINK® 2000 Crosslinking Agent (Cytec Industries, Inc., West Paterson, NJ), and the commercially available carboxyl functional backbone resin, XC-4005 acrylic resin (Cytec Industries Inc., West Patterson, NJ), along with 4% 4-dimethylaminopyridine (DMAP) catalyst as a 20 wt% solution in 1:1 xylene/isopropanol and 1:1:1 xylene/MIBK/ARCOSOLV PM Acetate (Arco Chemical, Philadelphia, PA) in the relative amounts shown in Table 4. The curable compositions were then applied to the substrate, iron phosphate treated cold roll steel panel, by using a #40 wire cator applicator, and subsequently cured at various cure temperatures ranging from 100°C to 140°C for 30 minutes.

30 The resulting coatings have physical properties shown in Table 5, in which the coatings exhibit increases in film hardness from 7.3 to 8.8 and increases in MEK rubs from

50/180 to 200+ as the curing temperature is increased from 100°C to 140°C.

Table 4: Curable Composition (Epoxy resin-TACT crosslinker and Carboxyl Functional Backbone Resin)

5	XC-4005 Acrylic Resin	37.3
	EPON Resin 825	7.0
	CYLINK® 2000 Crosslinking Agent	10.0
10	4-Dimethylaminopyridine, 20 wt % in 1:1 xylene/isopropanol	4.0
	1:1:1 ratio of Xylene/methyl isobutyl ketone/ARCOSOLV PM Acetate	7.0
15	Substrate	Iron phosphate treated cold roll steel panel
	Cure Schedule	100-140°C for 30 minutes

Table 5: Physical Properties of Curable Composition

20	Cure Schedule	100 °C/30 min	110 °C/30 min	125 °C/30 min	140 °C/30 min
	Film Thickness, mm	1.7	1.7	1.7	1.7
25	Film Hardness, KHN ₂₅	7.3	8.2	8.6	8.8
	MEK rubs	50/180	200+	200+	200+

EXAMPLE 4: Curable Compositions of Epoxy resin-TACT Crosslinker and Hydroxy Functional Polyester Backbone Resin

The curable composition containing a hydroxy functional polyester backbone resin was prepared by combining 5 the low molecular weight epoxy resin, HELOXY Modifier 48 (Shell Chemical Company, Houston, TX), CYLINK® 2000 Crosslinking Agent (Cytec Industries, Inc., West Paterson, NJ), and the commercially available hydroxy polyester functional backbone resin, McWhorter 72-7289 polyester resin, 10 along with 5% 4-dimethylaminopyridine (DMAP) catalyst as a 20 wt % solution in 1:1 xylene/isopropanol (DC#57 in 10 % n-butanol), and 1:1 xylene/ARCOSOLV PM Acetate in the relative amounts shown in Table 6. The curable composition was then applied to the substrate, iron phosphate treated cold roll steel panel, by using a #40 wire cator applicator, and 15 subsequently cured at cure temperatures 125°C and 140°C for 30 minutes. The resulting coating has physical properties shown in Table 7.

20 Table 6: Curable Composition (Epoxy resin-TACT crosslinker and Hydroxy Functional Backbone Resin)

McWhorter 72-7289 Polyester Resin	61.7
HELOXY Modifier 48	19.5
CYLINK® 2000 Crosslinking Agent	68.5
4-Dimethylaminopyridine, 20 wt % in 1:1 xylene/isopropanol	5.0
25 DC#57, 10% in butanol	0.5
1:1 ratio of Xylene/ARCOSOLV PM Acetate	24.8
Substrate	Iron phosphate treated cold roll steel panel
30 Cure Schedule	100-140°C for 30 minutes

Table 7: Physical Properties of the Curable Compositions

Cure Schedule	125 °C/30 min	140 °C/30 min
Film Thickness, mm	1.3	1.3
Film Hardness, KHN ₂₅	16.0	17.4
MEK rubs	75/200+	100/200+

EXAMPLE 5: Comparison of Curing In the Presence and
Absence of a Catalyst

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The 4-dimethylaminopyridine (DMAP)-catalyzed curing of a curable composition containing an epoxy resin-TACT crosslinker and a hydroxyl functional acrylic backbone resin was compared with the non-catalyzed curing and the results

15 are shown in Table 8.

Table 8 Catalyzed Curing of Curable Composition Containing Hydroxyl Backbone Resin

	A	B
S18510-63 Acrylic Resin	76.4	76.4
CYLINK® 2000 Crosslinking Agent	59.4	59.4
HELOXY Modifier 48	16.9	16.9
DMAP, 20 wt % in 1:1 xylene/propanol	5.0	0
DC#57, 10 wt % in n-butanol	0.5	0.5
1:1:1 Xylene/MIBK/ARCOSOLV PM Acetate	10.0	15.0

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	Substrate	Iron phosphate treated cold roll steel panel	Iron phosphate treated cold roll steel panel
5	Cure Schedule	100-140°C for 30 minutes	100-140°C for 30 minutes

S18510-63 Acrylic Resin is available from Cytec Industries Inc., West Patterson, NJ.

HELOXY Modifier 48 is commercially available from Shell Chemical Company, Houston.

DC#57 is commercially available from Dow Corning Corp., Midland, MI.

ARCOSOLV PM Acetate is commercially available from Arco Chemical, Philadelphia, PA

Table 9: Physical Properties of the Curable Composition A

Cure Schedule	100 °C/30 min	110 °C/30 min	125 °C/30 min
Film Thickness, mm	1.6	1.5	1.5
Film Hardness, KHN ₂₅	6.0	13.7	14.8
MEK rubs	1/50	5/200+	100/200+

20 Table 10: Physical Properties of the Curable Composition B

Cure Schedule	100 °C/30 min	110 °C/30 min	125 °C/30 min
Film Thickness, mm	1.6	1.5	1.4
Film Hardness, KHN ₂₅	1.0	8.2	14.8
MEK rubs	1/20	5/50	20/200+

The curable compositions were applied onto iron phosphate treated cold roll steel and cured at cure temperatures of 100°C, 110°C, and 125°C for 30 minutes. This formulation (A) contains DMAP catalyst according to the present invention and the physical properties are tabulated

in Table 9. It cures very well at 110°C for 30 minutes, as shown by a Knoop hardness of 13.7 and MEK rubs of 5/200+. At a curing temperature of 125°C, the film shows a Knoop hardness of 14.8 and MEK rubs of 100/200+. A comparative formulation (B) contains no catalyst and does not cure well at 110°C as shown by a Knoop hardness of 8.2 and MEK rubs of 15/50, tabulated in Table 10. It requires a higher temperature to cure, where a Knoop hardness of 14.8 and MEK rubs of 20/200+ are achieved when cured at 125°C for 30 minutes.

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EXAMPLE 6: Automotive Coatings

The coatings of the present invention may be applied to original equipment manufacturing (OEM) finish, including automotive, can, coil, and general coating applications. In this example, a black or white base coat was applied over an ED-5050 primed panel (Advanced Coating Technologies Labs, Hillsdale, MI). The base coat was baked at 90°C for 20 minutes and the clear top coat was applied over the base coat and baked at 140°C for 30 minutes. Table 11 lists the clear coat formulations tested, in which the test formulation (A) contains an epoxy resin-TACT crosslinker and the comparative formulation (B) contains CYMEL 303 automotive coatings (Cytec Industries Inc., West Patterson, NJ). Table 12 lists the formulation of white and black base coats. For the acid etch test evaluation, the black base coat was used. For other durability tests, such as QUV, Xenon acceleration, and Cleveland humidity resistance test, the white base coat was used.

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Table 11 Formulation of Clear Top Coatings

	A	B	
5	S18510-72 Acrylic Resin (Cytec Industries Inc., West Patterson, NJ)	76.3	100
10	HELOXY Modifier 48	16.9	0
15	CYLINK® 2000 Crosslinking Agent	59.4	0
20	CYMEL 303	0	30
25	DMAP, 20 wt % in 1:1 xylene/isopropanol	2.5	0
30	Dodecyl benzenesulfonic acid, 7 wt % in n-butanol	0	10.0
	CYAGARD UV-2337 Light Stabilizer (Cytec Industries Inc., Stamford, CT)	2.0	2.0
	SANDUVOR 3055 Light Stabilizer (Clariant Corp., Charlotte, NC)	1.0	0
	SANDUVOR 3058 Light Stabilizer (Clariant Corp., Charlotte, NC)	0	1.0
	DC#57, 10 % in n-butanol	0.5	0.5
	1:1:1 xylene/MIBK/ARCOSOLV PM Acetate	42.0	47.0

CYAGARD UV-2337 Light Stabilizer is commercially available from Cytec Industries Inc., Stamford, CT)

SANDUVOR 3055 and SANDUVOR 3058 Light Stabilizers are commercially available from Clariant Corp., Charlotte, NC.

DC#57 is commercially available from Dow Corning Corp., Midland, MI.

ARCOSOLV PM Acetate is commercially available from Arco Chemical, Philadelphia, PA

Table 12: Formulations of Base Coats

Base Coat	White	Black
3-Roll mill ground TiO ₂ , base ^A , 92 %	223.7	0
UCD 1524 HS Color Dispersion	0	22.9
ACRYLOID AT-400	25.0	85.5
CYTEL 325 Resin	28.0	30.4
CYTEL 247-10 Resin	4.0	3.4
Isopropanol	15.0	15.0
1:1:1 xylene/MIBK/ARCOSOLV PMA	90.0	45.0

Note A: This pigment grind contains 2 parts of TIPURE R-960 TiO₂ and 1 part

ACYRLOID AT-400 acrylic resin. TIPURE is a trademark of DuPont Chemical Company, Wilmington, DE.

15 UCD 1524 HS is commercially available from Morton International Inc., Chicago, IL.

ACYRLOID AT-400 is commercially available from Rohm & Haas Company, Philadelphia, PA.

CYTEL 325 and 247-10 Resins are commercially available from Cytec Industries Inc., West Patterson, NJ.

20 Table 13: Acid Etch Resistance Test (Exterior Exposure)

Clear Top Coating	A	B
Crosslinker	Epoxy/TACT	CYTEL 303
Etch Resistance Rating (0 = best, 10 = worst)	1	5

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Table 13 shows that the clear top coating containing the epoxy resin-TACT crosslinker gave a higher rating than the clear top coating containing CYTEL 303 resin in the acid etch resistance test, in which the coated ED-5050 panels were exposed outdoors for a period of one summer.

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Table 14: Cleveland Humidity Resistance at 60°C, 20°
Gloss/Blistering

Clear Top Coating	A	B
Crosslinker	Epoxy/TACT	CYMER 303
5 Gloss/Blistering Reading at 0 hours	91/10	90/10
Gloss/Blistering Reading at 479 hours	91/9F	89/2F
10 Gloss/Blistering Reading at 1173 hours	90/9F	89/2M
Gloss/Blistering Reading at 1486 hours	90/9F	89/1M
Gloss/Blistering Reading at 1842 hours	90/9M	87/1M

15 Table 14 shows that the clear top coating containing the epoxy resin-TACT crosslinker composition has higher humidity resistance than the clear top coating containing CYMER 303 resin. The humidity resistance was measured by two values, the gloss reading and the degree of 20 blistering of the coatings. ASTM D714-87. The first value is the gloss reading, and higher values indicate higher gloss, which is more desirable. The gloss readings were higher over time for the clear top coating containing the epoxy resin-TACT crosslinker. The second value is an index that measures the size of the blistering, and the letters F and M designate fine and medium blisters respectively. The lower the blister reading, the larger the blister. The 25 blister readings showed lower extent of blistering over time for the clear top coating containing the epoxy resin-TACT crosslinker.

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Table 15: QUV Resistance, 20° Gloss

Clear Top Coating	A	B
Crosslinker	Epoxy/TACT	CYTEL 303
Gloss Reading at 0 hours	92	90
Gloss Reading at 496 hours	91	90
Gloss Reading at 1212 hours	91	90
Gloss Reading at 1663 hours	89	90
Gloss Reading at 2120 hours	87	89

5

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Table 16: Xenon Accelerated Weathering Resistance, 20° Gloss

Clear Top Coating	A	B
Crosslinker	Epoxy/TACT	CYTEL 303
Gloss Reading at 0 hours	92	90
Gloss Reading at 560 hours	89	89
Gloss Reading at 1091 hours	79	79
Gloss Reading at 1527 hours	77	79
Gloss Reading at 1962 hours	80	78

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After about 2000 hours of exposure, the clear top coating containing the epoxy resin-TACT crosslinker has QUV resistance (Table 15) and Xenon accelerated weathering resistance (Table 16) that are as good as the clear top coating containing CYTEL 303.

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Example 7:**Waterborne Curable Compositions of TACT****Crosslinkers**

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Waterborne curable compositions containing TACT crosslinker were prepared by combining the low molecular weight epoxy resin, Heloxy Modifier 48 (Shell Chemical Company, Houston, Texas), CYLINK® 2000 Crosslinking Agent

(Cytec Industries, Inc., West Paterson, NJ), and, optionally, 0.1% of a 20 wt% solution of 4-dimethylaminopyridine (DMAP) catalyst to form a premix, then adding the premix to an acrylic emulsion polymer, Joncrys[®] 540 acrylic emulsion (S.C. Johnson Polymer, Racine, Wisconsin), and adjusting the viscosity with water. The relative amounts used are shown in Table 17. Two control batches containing no TACT crosslinker were prepared, one control containing DMAP catalyst, the second control containing no DMAP catalyst.

The compositions containing TACT in the formulation demonstrated much higher film hardness and better solvent resistance cure than the examples which did not contain TACT crosslinker.

Table 17

Example	1	2	3	4	5
Joncrys [®] 540 acrylic emulsion ¹	34.4	34.4	34.4	34.4	40.0
CYLINK [®] 2000 Crosslinking Agent	5.8	5.8	0	0	4.0
Heloxy [®] Modifier 48 ²	1.6	1.6	1.6	1.6	0
4-dimethylaminopyridine	0.1	0	0.1	0	0
Water	6.7	7.2	5.5	5.5	5.0
Substrate: treated aluminum panel					
Cure schedule: 125° C for 30 minutes					
Film thickness: 1.5 - 1.6 mils					
Knoop harness, KHN ₂₅	11.1	10.9	5.0	4.8	10.5
MEK rubs	150	200	15	15	60

Note 1: Joncrys[®] is a trademark of S.C. Johnson Polymer, Racine, Wisconsin.

Note 2: Heloxy[®] is a trademark of Shell Chemical Company, Houston, Texas. The chemical name of Heloxy Modifier 48 is trimethylol propane triglycidyl ether.

The coating performance of the TACT waterborne system was improved by the presence of Heloxy Modifier 48 (Shell Chemical Company, Houston, Texas) in the formulation, as demonstrated in Table 18.

5

Table 18

<i>Example</i>	6	7	8	9
Joncryl® 540 acrylic emulsion	20.62	22.34	23.32	24.0
CYLINK® 2000 Crosslinking Agent	3.47	2.82	2.45	2.4
Heloxy® Modifier 48	0.99	0.53	0.28	0
Water	4.92	4.30	3.95	3.60
Substrate: treated aluminum panel				
Cure schedule: 125° C - 140° for 30 minutes				
Film thickness: 1.5 - 1.6 mils				
<u>125°C/30 min bake</u>				
Knoop hardness, KHN ₂₅	10.2	11.7	12.4	13.6
MEK rubs	140	80	50	50
<u>140°C/30min bake</u>				
Knoop hardness, KHN ₂₅	11.0	12.4	11.1	14.6
MEK rubs	200+	100	70	50

Example 8:**Comparison of Waterborne TACT Crosslinker****25 Composition to Conventional Amino-based Waterborne Systems**

Current amino-based waterborne systems are capable of fast cure and exhibit good film properties such as hardness with flexibility and humidity resistance. Such amino-based waterborne systems, however, emit formaldehyde on 30 curing.

As demonstrated in table 19, the waterborne TACT crosslinker composition has improved curing response, results in a harder film and has better impact resistance than CYMEL® 303 Resin (Cytec Industries, Inc., west Patterson, NJ).

5

Table 19

<i>Example</i>	10	11
Joncryl® 540 acrylic emulsion	68.72	100.0
CYLINK® 2000 Crosslinking Agent	11.57	0
Heloxy® Modifier 48, 80% in butanol	4.11	0
CYMEL® 303 Resin ³ , 50% in butanol	0	30.0
CYCAT® 4045 Catalyst ⁴	0	0.75
Water	15.6	20.0
Substrate: treated aluminum panel		
Cure schedule: 140° C for 30 minutes		
Film thickness: 1.5 - 1.6 mils		
Knoop harness, KHN ₂₅	11.9	5.3
MEK rubs	200+	150/200
T-bend	2T	2T
Direct impact, in-lb.	50	30
Reverse impact, in-lb.	30	<10

Note 3: CYMEL® is a product of Cytec Industries Inc., W. Paterson, NJ.

Note 4: CYCAT® is a product of Cytec Industries Inc., W. Paterson, NJ.

Similar results are obtained when the two systems are baked at high temperature and short cure time, as demonstrated in Table 20.

30

Table 20

Example	12	13
Joncryl® 540 acrylic emulsion	68.72	100.0
CYLINK® 2000 Crosslinking Agent	11.57	0
Heloxy® Modifier 48, 80% in butanol	4.11	0
CYMEL® 303 Resin, 50% in butanol	0	30.0
CYCAT® 4045 Catalyst	0	0.75
Water	15.6	20.0
Substrate: treated aluminum panel		
Cure schedule: 190° C for 120 Seconds		
Film thickness: 0.7 - 0.8 mils		
Knoop hardness, KHN ₂₅	14.6	11.3
Pencil hardness	2H - 3H	H - 2H
MEK rubs	200+	100/200
T-bend	2T	2T
Direct impact, in-lb.	60+	60+
Reverse impact, in-lb.	30	10

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Further, the waterborne TACT crosslinker composition has better humidity resistance than CYMEL® 303 or CYMEL® 1123 Resins (Cytec Industries, Inc., west Patterson, NJ), as demonstrated in Table 21.

Table 21

<i>Example</i>	14	15	16
Joncryl® 540 acrylic emulsion	44.67	40.0	40.0
CYLINK® 2000 Crosslinking Agent	7.52	0	0
Heloxy® Modifier 48, 80% in butanol	2.67	0	0
CYMEL® 303 Resin, 80% in butanol	0	7.5	0
CYMEL® 1123 Resin, 80% in butanol	0	0	7.5
CYCAT® 4045 Catalyst, 10% in water	0	3.0	3.0
Water	3.0	3.0	3.0
Substrate: treated aluminum panel			
Cure schedule: 190° C for 120 seconds			
Film thickness: 0.7 - 0.8 mils			
Knoop hardness, KHN ₂₅	14.3	5.7	6.5
MEK rubs	200+	100/200+	10/150
Cleveland humidity resistance at 60°C			
Blistering, After 1 day	10	9/F	10
After 15 days	10	6/M	10
Appearance, After 1 day	Clear	Slightly hazy	Hazy
After 15 days	Clear	Slightly hazy	Hazy

Example 9: Use of Aromatic Epoxy Resins in Waterborne TACT crosslinker Compositions

Aromatic low molecular weight epoxy resins may be utilized in the waterborne TACT crosslinker compositions. As demonstrated in Table 22, the system containing the aromatic epoxy resin, Epon® 825 (Shell Chemical Company, Houston, Texas) exhibited a shorter pot life than a system containing an aliphatic epoxy resin.

10 Table 22

Example	17	18
Joncryl® 540 acrylic emulsion	44.67	40.4
CYLINK® 2000 Crosslinking Agent	7.52	6.8
15 Heloxy® Modifier 48, 80% in butanol	2.67	0
Epon® 825 ⁵ , 80% in butanol	0	3.0
Water	3.0	9.77
Pot life	>30 days	<3 days
Substrate: treated aluminum panel		
20 Cure schedule: 190° C for 120 seconds		
Film thickness: 0.7 - 0.8 mils		
<u>170°C/120" Bake</u>		
Knoop harness, KHN ₂₅	13.0	13.0
MEK rubs	20/150	20/100
<u>180°C/120" Bake</u>		
Knoop harness, KHN ₂₅	14.6	13.6
MEK rubs	50/200+	25/200

Note 5: Epon® is a trademark of Shell Chemical Company, Houston, Texas.

Example 10: Curable compositions of Polyester resin -TACT Crosslinker and Hydroxy Functional Polyester Backbone Resin

The curable composition containing a hydroxy functional polyester backbone resin was prepared by combining the Chempol ® 11-1369 Polyester Resin (Cook Composites and Polymers, Port Washington, WI) along with 5% 4-dimethylaminopyridine (DMAP) catalyst as a 20 wt % solution in 1:1 xylene/isopropanol (DC#57 in 10 % n-butanol in the relative amounts shown in Table 23. The curable composition was then applied to the substrate, iron phosphate treated cold roll steel panel, by using a #40 wire cator applicator, and subsequently cured at cure temperatures 125°C and 140°C for 30 minutes.

The resulting coating has physical properties also shown in Table 23. Formulations A and B which contain TACT and epoxy resin demonstrate superior MEK solvent resistance and Cleveland humidity resistance than Formulation C which contains only TACT crosslinker.

Table 24 demonstrates that polyester resins with high acid number demonstrate superior MEK solvent resistance in the TACT-epoxy-polyol system.

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Table 23
Cure Response of TACT Polyester Coating Systems

5	Substrate: Iron phosphate treated cold roll steel			
	Cure schedule: 140°C for 30 minutes			
	Film thickness: 30µm			
		A TACT/EPOXY	B TACT/EPOXY	C TACT
	Chempol® 11-1369 Polyester Resin	45.0	55.4	72.0
	CYLINK® 2000 Crosslinking Agent	35.1	32.4	28.0
	Heloxy® Modifier 48	19.9	12.3	0
	4-Dimethylaminopyridine	0.3	0.3	0
	OH/Carbamate/Epoxy mole ratio	1/1/2	1/1.5/0.5	1/1/0
	Tukon hardness, KHN ₂₅	16.9	14.9	13.7
10	MEK Rubs	200+	200+	50/200
	Cleveland humidity resistance, 60°C			
	20°/60° Gloss	0 hours	97/101	96/101
		24 hours	96/100	96/100
		96 hours	95/100	95/100
15	Blistering	24 hours	10	10
		96 hours	10	9VF
20				

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Table 24

Cure Response of TACT Polyester Coating Systems (Effect of Acid Number of Polyester Resin)

5	Substrate: Iron phosphate treated cold roll steel Cure schedule: 125 - 140°C for 30 minutes		
		D	E
	Polymac® HS 57-5789 Polyester Resin	48.6	0
	Polymac® WR 72-7289 Polyester Resin	0	46.3
10	CYLINK® 2000 Crosslinking Agent	32.8	34.2
	Heloxy® Modifier 48	18.6	19.5
	DMAP	1	1
	OH/Carbamate/Epoxy mole ratio	1/2/1	1/2/1
	<u>125°C for 30 minutes</u>		
15	Film thickness, µm	43	33
	Film hardness, KHN ₂₅	16.9	16
	MEK rubs	20/200+	75/200+
	<u>140°C for 30 minutes</u>		
20	Film thickness, µm	43	33
	Film hardness, KHN ₂₅	20.6	17.4
	MEK rubs	50/200+	100/200+

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Example 11: Shelf Life of TACT Waterborne Coating

Cure responses of fresh samples and samples aged for 10 weeks at room temperature were compared. As demonstrated in Table 25, the responses were very similar.

30 The only film deficiency is the 50 MEK double rubs resistance or low crosslinking density. This is because Joncryl® 540

acrylic emulsion polymer is designed for amino formaldehyde resins, and has an acid number of 50 and a hydroxyl number of 42.

5 Table 25

Shelf Life of TACT Waterborne Coating

System: Joncryl 540® Acrylic Emulsion Polymer / TACT = 90/10 Substrate: ACT ² Aluminum 5052H32 04X12X025 Film thickness: 35-40 µm Cure schedule: 140°C for 30 minutes				
		<u>Knoop Hardness</u>		
		<u>Fresh</u>	<u>Aged</u>	MEK Rubs
1 wks		9.8	10.2	9.8
3 wks		9.7	9.9	9.7
6 wks		12.8	13.0	12.8
10 wks		10.3	10.1	10.3

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Note 2 ACT Laboratories, Inc., Hillsdale, MI, USA.

Example 12: Cure Response of TACT Acrylic Emulsion Coating Systems

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Table 26 lists examples of adding an undiluted low viscosity epoxy resin to enhance the performance of the acrylic emulsion system. Formulation-F contains both TACT and epoxy resin. Formulation-G contains the epoxy resin, and Formulation-H contains TACT only. On the 140°C cure schedule, Formulation-G resulted in only 20 MEK double rubs resistance. Formulation-H was slightly better with 50 MEK double rubs resistance. Formulation-G gave more than 100 MEK double rubs resistance. This demonstrates that the combination of TACT and tri-functional epoxy resin leads to a synergistic cure response effect for the acrylic emulsion polyol coating formulation.

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The formaldehyde free system, Formulation-F was also compared to a typical can coating formulation based on CYMEL® 303 Crosslinking Agent on a 180°C/5 minute cure schedule. Can coating performances are compared in Table 27.

5 The new TACT/epoxy system exhibits the same 3-4H pencil film hardness as CYMEL 303 resin, while demonstrating improved flexibility, rub resistance and retort resistance (tested at 121°C for 30 minutes).

Table 26

10 Cure Response of TACT Acrylic Emulsion Coating Systems

Substrate: ACT Aluminum 5052H32 04X12X025 Cure schedule: 140°C for 30 minutes Film thickness: 40µm				
		F TACT/Epoxy	G Epoxy Resin	H TACT
15	Joncryl® 540 Acrylic Emulsion Polymer	77.3	77.3	90.0
	CYLINK® 2000 Crosslinking Agent	14.5	0	10.0
	Heloxy® Modifier 48	8.2	8.2	0
	<u>140°C/30min</u>			
20	Tukon hardness, KHN ₂₅	11.1	4.8	10.3
	MEK rubs	100+	20	50

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Table 27
Can Coating Performances of TACT Acrylic Emulsion Coating Systems

5	Substrate: ACT Aluminum 6061T6 04X12X032		
	Cure schedule: 180°C for 5 minutes		
	Film thickness: 7.6 µm		
		<u>F</u>	<u>I</u>
		<u>Heloxy/TACT</u>	<u>CYMEL 303</u>
	Joncryl® 540 Acrylic Emulsion Polymer	77.3	75.0
10	CYLINK® 2000 Crosslinking Agent	14.5	0
	Heloxy® Modifier 48	8.2	0
	CYMEL® 303 Crosslinking Agent	0	25.0
	CYCAT® 4045 Catalyst	0	0.4
	Viscosity ³ (35% non-volatile at 25°C), mPa.s.		
15	1 day	38	15
	2 days	48	14
	5 days	93	15
	Pencil Hardness	3-4H	3-4H
	20°/60° Gloss	88/159	91/152
20	MEK Rubs	200+	125/200+
	Adhesion, (ASTM D 3359-93)	5	5
	Reverse Impact, inch-lb	80	40
	Retort Resistance, 121°C for 30 minutes		
25	20°/60° Gloss	67/143	53/131
	Adhesion	5	5
	MEK Rubs	50/200	45/100
	Appearance	OK	Micro size water spots

Note 3 Cone & Plate Viscometer and spindle #40.

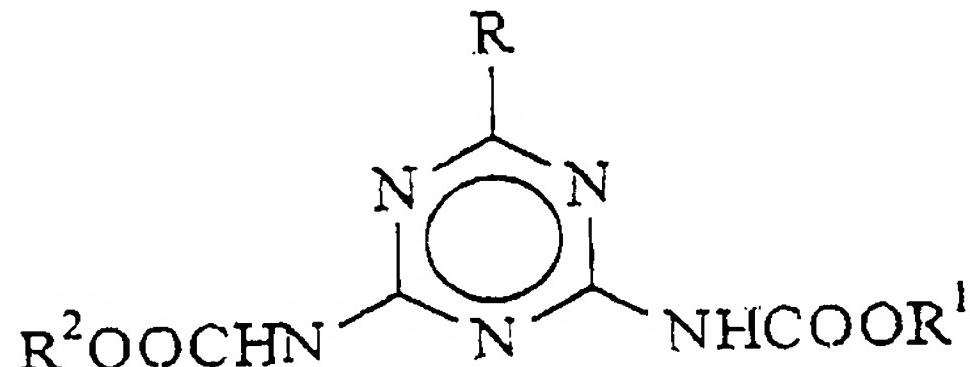
THE CLAIMS

what is claimed is:

1. A crosslinking composition, comprising:

(1) a 1,3,5 triazine carbamate of the

5 following general formula, as well as oligomers thereof:



10 wherein R is selected from the group consisting of -NHCOOR³,

hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbyloxy

hydrocarbyl, hydrocarbylthio, amido, sulfonamido, amino,

hydrocarbylamino, dihydrocarbylamino, cyclic amino and

hydrocarbyleneamino; and wherein each R¹, R² and R³ is

15 independently selected from the group consisting of

hydrocarbyl and hydrocarbyloxy hydrocarbyl; and

(2) a resin component comprising a

polyfunctional epoxy compound containing, on average, at

least two epoxy functionalities per molecule, such

polyfunctional compound being a low molecular weight glycidyl

20 ether epoxy compound.

2. The crosslinking composition of claim 1,

wherein R is -NHCOOR³, and R¹, R² and R³ are the same or

different and each is an alkyl group of 1 to 8 carbon atoms.

25

3. The crosslinking composition of claim 2,

wherein R¹, R² and R³ are the same or different and each is

butyl or methyl, and the methyl to butyl molar ratio is from

about 0.5 to about 1.5.

4. The crosslinking composition of claim 1, wherein the polyfunctional epoxy compound has a molecular weight of from about 100 g/mol to about 2000 g/mol.

5

5. A curable composition, comprising:

(1) the crosslinking composition of claim 1;

and

(2) a backbone resin selected from the group consisting of a polyfunctional hydroxy group containing material, a polyfunctional carboxyl group containing material 10 and a polyfunctional hydroxyl and carboxyl group containing material.

15

6. The curable composition of claim 5, wherein the polyfunctional hydroxy group containing material is selected from the group consisting of polyols, alkyds, hydroxyfunctional acrylic resins, hydroxyfunctional polyester resins, hydroxyfunctional polyurethane prepolymers, products derived from condensation of epoxy resins with an amine, and mixtures thereof.

20

7. The curable composition of claim 5, wherein the polyfunctional carboxyl group containing material is selected from the group consisting of acrylic carboxy compounds and polyester carboxy compounds.

25

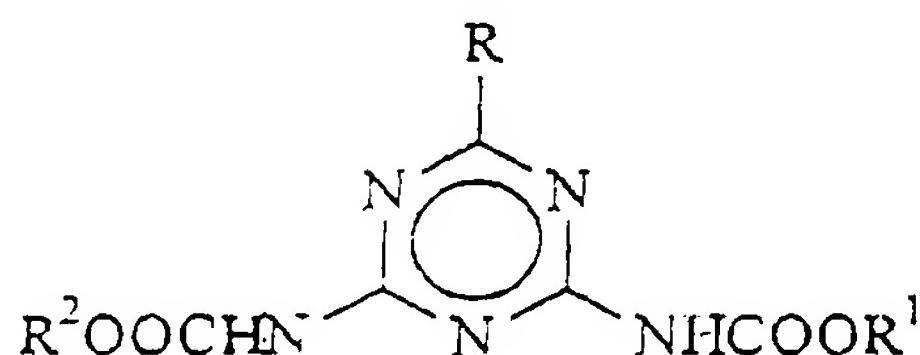
8. The curable composition of claim 5, wherein the crosslinker component further comprises a base cure catalyst selected from the group consisting of a quaternary ammonium salt, a quaternary phosphonium salt, a strong nitrogenous base, an inorganic base and mixtures thereof.

30

9. A curable emulsion composition, comprising:

(1) a crosslinker composition comprising a 1,3,5 triazine carbamate of the following general formula, as well as oligomers thereof:

5



wherein R is selected from the group consisting of -NHCOOR³, hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbyloxy hydrocarbyl, hydrocarbylthio, amido, sulfonamido, amino, hydrocarbylamino, dihydrocarbylamino, cyclic amino and hydrocarbyleneamino; and wherein each R¹, R² and R³ is independently selected from the group consisting of hydrocarbyl and hydrocarbyloxy hydrocarbyl;

15

- (2) water; and
- (3) a polyfunctional hydroxy group containing material.

10. The crosslinking composition of claim 9, wherein R is -NHCOOR³, and R¹, R² and R³ are the same or different and each is an alkyl group of 1 to 8 carbon atoms.

11. The crosslinking composition of claim 10, wherein R¹, R² and R³ are the same or different and each is butyl or methyl, and the methyl to butyl molar ratio is from about 0.5 to about 1.5.

25

12. The crosslinking composition of claim 9, wherein the polyfunctional epoxy compound has a molecular weight of from about 100 g/mol to about 2000 g/mol.

30

13. The curable composition of claim 9, wherein the polyfunctional hydroxy group containing material is

selected from the group consisting of polyols, alkyds, hydroxyfunctional acrylic resins, hydroxyfunctional polyester resins, hydroxyfunctional polyurethane prepolymers, products derived from condensation of epoxy resins with an amine, and mixtures thereof.

5

14. The curable composition of claim 9, wherein the crosslinker component further comprises a resin component comprising a polyfunctional epoxy compound containing, on average, at least two epoxy functionalities per molecule, 10 such polyfunctional compound being a low molecular weight glycidyl ether epoxy compound

15. The curable composition of claim 14 , wherein the crosslinker component further comprises a base cure catalyst selected from the group consisting of a quaternary ammonium salt, a quaternary phosphonium salt, a strong 15 nitrogenous base, an inorganic base and mixtures thereof.

20

16. The curable composition of claim 5, in the form of a liquid coating composition.

17. The curable composition of claim 16, wherein the liquid coating composition is a water-borne coating composition or a solvent-borne coating composition.

25

18. The curable composition of claim 5, in the form of a powder coating composition.

30

19. The crosslinker composition of claim 1, wherein the epoxy component and the triazine carbamate component are present in an epoxy: carbamate equivalents ratio of from about 0.5:1 to about 2:1.

20. The curable composition of claim 9, wherein the solids content is from about 20 weight percent to about 75 weight percent.

5 21. A method of coating a substrate, comprising the steps of:

(A) applying to the substrate a curable composition comprising:

(1) the crosslinking composition of claim 1; and

10 (2) a backbone resin selected from the group consisting of a polyfunctional hydroxy group containing material, a polyfunctional carboxyl group containing material and a polyfunctional hydroxyl and carboxyl group containing material; then

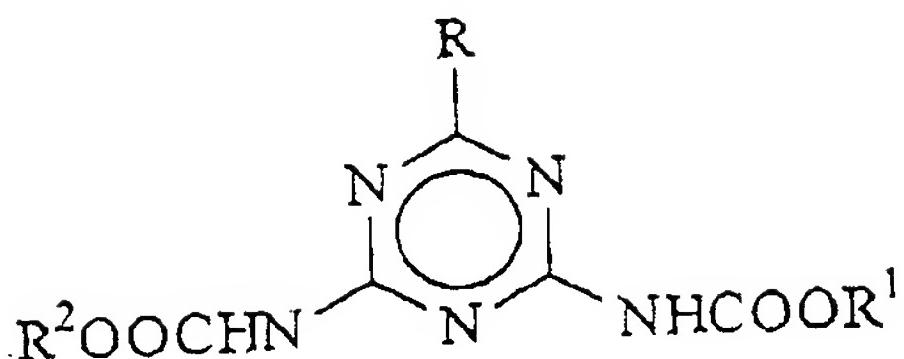
15 (B) curing the so applied curable composition to form a crosslinked film.

22. The method of claim 21, wherein the crosslinker component further comprises a base cure catalyst selected from the group consisting of a quaternary ammonium salt, a quaternary phosphonium salt, a strong nitrogenous base, an inorganic base and mixtures thereof.

23. A method of coating a substrate, comprising the steps of:

25 (A) applying to the substrate a curable composition comprising:

(1) a crosslinker composition comprising a 1,3,5 triazine carbamate of the following general formula, as well as oligomers thereof:



5 wherein R is selected from the group consisting of -NHCOOR³, hydrogen, hydrocarbyl, hydrocarbyloxy, hydrocarbyloxyhydrocarbyl, hydrocarbylthio, amido, sulfonamido, amino, hydrocarbylamino, dihydrocarbylamino, cyclic amino and hydrocarbyleneamino; and wherein each R¹, R² and R³ is independently selected from the group consisting of hydrocarbyl and hydrocarbyloxy hydrocarbyl;

10 (2) water; and

(3) a polyfunctional hydroxy group containing material; then

(B) curing the so applied curable composition to

15 form a crosslinked film.

24. The method of claim 23, wherein the crosslinker component further comprises a resin component comprising a polyfunctional epoxy compound containing, on average, at least two epoxy functionalities per molecule,

20 such polyfunctional compound being a low molecular weight glycidyl ether epoxy compound.

25. The method of claim 24, wherein the crosslinker component further comprises a base cure catalyst selected from the group consisting of a quaternary ammonium salt, a quaternary phosphonium salt, a strong nitrogenous base, an inorganic base and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
 PCT/US 00/32706

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08K5/3492 C09D157/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C08K C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 852 133 A (WU KUANG JONG ET AL) 22 December 1998 (1998-12-22) cited in the application claims; examples ---	1-4, 9, 10, 13, 15-17, 23
X	WO 97 08235 A (CYTEC TECH CORP) 6 March 1997 (1997-03-06) claims; examples ---	1-4, 9, 10, 13, 15-17, 23
X	WO 98 02495 A (BASF LACKE & FARBEN ;LUEER INGO (DE); NOF CORP (JP); NUKITA AKITO) 22 January 1998 (1998-01-22) page 15, line 25 -page 16, line 10; claims; examples 1-5; tables 1,2 ---	9, 10, 13, 15-17, 23

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

5 March 2001

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INTERNATIONAL SEARCH REPORT

Int	tional Application No
PCT/US 00/32706	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/32706

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